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Chemical Abstracts, Derwent WPI, Claims

(71) Applicant

Mitsubishi Metal Corporation

(Incorporated in Japan)

5-2, Otemachi 1-chome, Chiyoda-ku, Tokyo, Japan

(74) Agent and/or Address for Service

Frank B Dehn & Co

Imperial House, 15-19 Kingsway, London, WC2B 6UZ,
United Kingdom

(72) Inventors

Motohiko Yoshizumi
Yukio Yamashita
Adira Nishihara
Akihiro Nakamura
Toshiharu Hayashi
Midori Kaneko
Kazuyoshi Murakami

(54) Perfluoroalkylsulphonamidoalkyl silanes; surface treatment agents

(57) N-alkyl-N-[3-(substituted-silyl) propyl] -perfluoroalkylsulfonamide compounds, such as $C_6 F_{17} SO_2 N(C_3 H_7) CH_2 CH_2 Si(OCH_3)_3$, are obtainable by (i) hydrosilylation of the corresponding alkyl sulphonamide or (ii) reacting appropriate perfluoroalkylsulphonamide and aminoalkylsilane compounds. The compounds have excellent water- and oil-repellency and serve as surface property improvers for various material e.g. fillers, pigments, paper, glass and metal.

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Title of the Invention

Novel fluorine-containing silane compounds, processes for preparing the same and uses thereof

Field of the Invention

5 This invention relates to a class of novel N-alkyl-N-[3-(substituted-silyl)propyl]-perfluoroalkylsulfonamide compounds, processes for preparing the same and uses thereof. The compounds of the present invention can be used as surface modifiers for various materials.

Background of the Invention

Silane compounds having a perfluoroalkyl group or groups are known and use thereof as mold release agents is being considered.

Recently, improvement of water-repellency, oil-repellency, non-tackiness of both resins and inorganic materials are desired.

15 Conventional silane compounds are not satisfactory in water-repellency, oil-repellency and non-tackiness when they are used as surface property improver.

20 Silane compounds having a perfluoroalkyl group or groups have good water- and oil-repellency but are still unsatisfactory in adhesion to substrate materials and thermal and chemical stability. Some of them have disadvantage in that starting materials for the preparation decompose during the hydrosilylation reaction for the synthesis thereof resulting in low yield of the product.

We conducted an extensive study in order to overcome the above-described problems and have found that certain silane compounds having a perfluoroalkyl group and a sulfonamide group in a molecule overcome the above problems and are suitable for the purpose of the present invention.

Summary of the Invention

30 This invention provides a class of novel N-alkyl-N-[3-(substituted-silyl)propyl]-perfluoroalkylsulfonamides represented by the formula



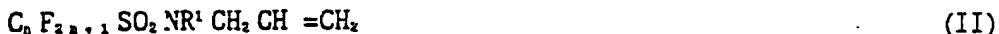
wherein R¹ is a C₁₋₈ alkyl group, R² is a C₁₋₈ alkyl group and A is chlorine or bromine or a C₁₋₈ alkoxy group, n is an integer of 4 to 12, m is an integer of 1 to 3.

Preferably, R¹ is C₁₋₈ alkyl, R² is C₁₋₈ alkyl, A is methoxy or ethoxy or chlorine, n is 6-10 and m is 3.

More preferably, R¹ is n-propyl, R² is methyl or ethyl, A is methoxy or ethoxy, n is 8 and m is 3.

This invention also provides processes for preparing the N-alkyl-N-[3-(substituted-silyl)propyl]-perfluoroalkylsulfonamides recited above.

The compounds of the present invention can be prepared by a process comprising reacting an N-allyl-N-alkyl-perfluoroalkylsulfonamide represented by the formula



wherein R¹ and n are as defined above, with a halo-, alkoxy- or haloalkoxysilane represented by the formula



wherein R², A and m are as defined above, in the presence of an addition catalyst; and further reacting the resulting addition product with a C₁₋₅ alcohol, if desired when A is chlorine or bromine.

The compounds of the formula (II) can be prepared by reacting a perfluoroalkylsulfonyl fluoride prepared by electrolytic fluorination with an N-alkylallylamine, or reacting perfluoroalkylsulfonyl fluoride with an N-alkylamine to form an N-alkylperfluoroalkylsulfonamide and thereafter reacting it with an allyl halide in the presence of an alkali.

These compounds are produced by New Akita Chemical Co., Ltd. (Shin-Akita Kasei Kabushiki Kaisha) and N-n-propyl-N-perfluorooctyl-allyl-sulfonamide is marketed by said company.

The compounds of the general formula (III) are also commercially available, from Tokyo Kasei Kabushiki Kaisha for instance.

In the process as recited above, the preferred addition catalysts are chloroplatinic acid, azo-bis-isobutyronitrile, benzoyl peroxide, an octacarbonyl complex of cobalt, platinum and rhodium.

In the process as recited above, the reaction of the addition product, of which A is chlorine or bromine, and a C₁₋₅ alcohol can preferably be conducted by blowing dry air into the reaction mixture or under a reduced pressure. The evacuation should be enough to remove formed hydrogen halide but not to be excessive lest it should cause loss of the used alcohol.

The reaction of the addition product, of which A is chlorine or bromine, and said alcohol also can preferably be conducted in the presence of a base such as organic amine.

The compounds of the present invention, of which A is C_{1-5} alkoxy, also can be prepared by reacting the addition product of the compound of the formula (II) and the compound of the formula (III) with a corresponding metal alkoxide.

5 The compounds of the present invention, of which A is C_{1-5} alkoxy, also can be prepared by reacting the addition product of the compound of the formula (II) and the compound of the formula (III) with an orthoformic acid ester of the corresponding alcohol.

10 The compounds of the present invention represented by the formula (I), wherein A is a C_{1-5} alkoxy group, can be prepared by a process comprising reacting a compound represented by the formula



wherein Y is fluorine, chlorine or bromine and n is as defined above, with an aminosilane represented by the formula



wherein R¹, R² and m are as defined above and A is as defined above.

In the compounds of the present invention represented by formula (I), the alkyl group R¹ may be straight-chained or branched.

20 A compound represented by formula (III) is used in an amount of 1 mole equivalent or more, preferably 1.3-1.5 mol per mole of the compound (II). The reaction of a compound of formula (II) and a compound of (III) is conducted at 30-150°C, preferably 40-80°C under agitation.

25 The amount of the catalyst to be used is usually 1×10^{-5} to $1 \times 10^{-3}\%$, preferably 1×10^{-4} to $5 \times 10^{-4}\%$ by weight of the amount of the compound of formula (II).

30 The reaction of a compound of formula (I), wherein A is chlorine or bromine, and a C_{1-5} alcohol can be easily conducted by blowing a dry inert gas into the reaction mixture at 5-40°C, preferably 10-20°C, or by stirring the reaction mixture under a reduced pressure.

The gas should be inert to the compound of formula (I) wherein A is chlorine or bromine and the C_{1-5} alcohol, specifically, dried N₂, He, Ar, etc. are preferred.

35 Blowing-in of the dry inert gas is made for removal of liberated HCl or HBr and evacuation has the same effect. If the pressure is reduced excessively, loss of the used alcohol by vaporization will occur.

When the compounds of the present invention reprented by the

formula (I), wherein A is a C_{1-6} alkoxy group, are prepared by the reaction of a perfluoroalkylsulfonyl chloride (compound of formula (IV)) and an aminosilane (compound of formula (V)), it is preferred that the former is used in an amount of more than 1 mole equivalent, preferably 1.05 or 1.2 moles, to the amount of the latter.

The reaction of the compound of formula (IV) and the compound of formula (V) is preferably conducted in the presence of an organic base such as pyridine, triethylamine, etc. in order to remove formed hydrogen halide.

Although it is not necessary to employ a solvent, a solvent inert to the reaction not specifically limited can be used. Specific examples of such solvents are ether compounds such as tetrahydrofuran, isopropylether, etc. Although the reaction temperature is varied in accordance with the species of the solvent employed, it is usually between room temperature and 100°C, preferably 20-50°C.

The sulfonamide moiety of the compounds of the present invention enhances the yield in the hydrosilylation in their synthesis and brings about better orientation of the perfluoroalkyl group more than carboxylic acid compounds or carboxylic amide compounds when used as a surface property modifier, and thus improves water-repellency, oil-repellency and non-tackiness of the substrate.

Further, the alkyl group bonded to the nitrogen atom promotes miscibility with organic solvents.

The compounds of this invention are useful as water- and oil-repellent, surface property modifier and for other various uses.

That is, this invention also provides filler powders or filler short fibers to the surface of which one of the above described silane compounds is bonded or adheres.

This invention also provides fluorine resin compositions containing an inorganic filler treated with one of the above recited silane compounds.

This invention also provides water- and oil-repellent paper and glass treated with or containing the above described silane compounds.

This invention also provides weathering-resistant construction materials the surface of which is treated with the above-described silane compounds.

This invention also provides water- and oil-repellent and non-

solderable electroconductive metallic materials, the surface of which is treated with one of the above-described silane compounds.

This invention also provides inorganic pigments and fillers which are treated with the above-described silane compounds and have good dispersibility in organic solvents and gives less viscous coating materials (paints).

The water-repellency, oil-repellency and non-tackiness of the compounds of the present invention is exhibited by the perfluoroalkyl group thereof and the halogen or alkoxy groups thereof react with water to be converted to hydroxysilyl groups, which combines with hydroxy groups existing on the surface of inorganic materials by dehydration condensation, hydrogen bond, etc.

When the compound of the present invention is applied to the surface of a material or incorporated therein, it is usually used as a solution in an organic solvent. The manner of the application and mixing is not specifically limited. Preferably, the compound is dissolved in an anhydrous chlorinated solvent, a fluorinated solvent, acetone, tetrahydrofuran, hexane, an alcohol and the like or a mixture thereof or those in which a small amount of an aqueous solution of an amine or acid is added, and the solution is applied to the object surface by a known method such as spraying, dipping, etc.

Specific Description of the Invention

Now the invention will be illustrated by way of working examples.

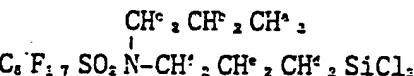
Example 1

In a 500ml three-necked flask equipped with a magnetic stirrer, a thermometer and a reflux cooler, 108.1g (0.200mol) of N-n-propyl-N-perfluorooctylsulfonamide ("EF-111" marketed by New Akita Chemical Co.), 15.4g of 85% potassium hydroxide (0.233mol) and 200ml of acetone were placed, and into this mixture, 30.71g (0.254mol) of allyl bromide was added dropwise over a period of 10 minutes at room temperature. After stirring was continued further for 4 hours, the reaction mixture was filtered, the filtrate was concentrated by distillation until the volume thereof was reduced to 100ml and was poured into a 5% ammonium chloride aqueous solution. The organic layer was collected, the vacuum distillation of which gave N-n-propyl-N-allyl-perfluorooctylsulfonamide.

Then, in a 100ml three-necked flask equipped with a magnetic stirrer, a thermometer and a reflux cooler, 96.9g (0.167mol) of the

above N-n-propyl-N-allyl-perfluoroctylsulfonamide and 5mg of a 0.1M isopropanol solution of chloroplatinic acid hexahydrate (9.67×10^{-3} mmol) were placed and 25.3ml (0.250mol) of trichlorosilane was added dropwise over a period of 30min.

Stirring was further continued for 2 hours after the addition of trichlorosilane was finished, and then the vacuum distillation of the reaction mixture gave 110.3g (0.1539mol) of N-n-propyl-N-[3-(trichlorosilyl)propyl]-perfluoroctylsulfonamide. Yield: 92.3%; B.P. 153°C/2.0mmHg. The compound was identified as:



by NMR analysis, MS analysis and IR spectrophotometric analysis.

Conditions and results of the NMR and MS analyses were as follows.

¹⁵ ¹H NMR analysis:

Solvent: Flon-113(1, 1, 2-trichloro-2, 2, 1-trifluoroethane),
Internal standard: benzene
 δ 1.30(t, 3H, H-a), δ 1.6-2.5(m, 6H, H-b, d, e), δ 3.5-4.0(m, 4H, H-c, f)

²⁰ MS analysis:

Ionization voltage: 70eV

m/e, relative intensity and moiety are as follows in this order: 554, 60.5%, $\text{M}^+ - \text{CH}_2\text{CH}_2\text{SiCl}_3$; 133, 15.0%, SiCl_3 , 69, 100%, CF_3

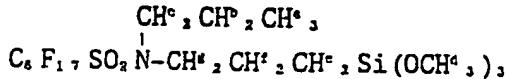
²⁵ IR spectrophotometry

Sample: neat

3350, 2950, 1390, 1260-1130 (cm^{-1})

Example 2

In a 300ml four-necked flask equipped with a mechanical stirrer, a trap, a thermometer and a reflux cooler to which an aspirator was connected, 48.1g (0.0671mol) of N-n-propyl-N-[3-(trichlorosilyl)-propyl]-perfluoroctylsulfonamide was placed and 50ml of methanol was added dropwise over a period of 2 hours at 15-20°C under a reduced pressure. Thereafter, vacuum distillation gave 40.1g (0.057mol) of N-n-propyl-N-[3-(trimethoxysilyl)propyl]-perfluoroctylsulfonamide. Yield: 85.0%; B.P. 134°C/0.25mmHg. The compound was identified as:



by NMR analysis, MS analysis and IR spectrophotometric analysis.

Conditions and results of analyses were as follows.

¹H NMR analysis:

Solvent: Flon-113, Internal standard: benzene

5 δ 0.9(t, 2H, H-e), 1.25(t, 3H, H-a), 1.6-2.5(m, 6H, H-b,
e, f), 3.5-4.0(m, 4H, H-c, g), 3.8(s, 9H, H-d)

MS analysis:

Ionization voltage: 70eV

10 m/e, relative intensity and moiety are as follows in
this order: 672, 22.6%, M⁺-OCH₃; 554, 1.8%, M⁺-
·CH₂CH₂Si(OCH₃)₃, 121, 100%, ·Si(OCH₃)₃; 69, 23%, ·CF₃

IR spectrophotometry:

Sample: neat

3350, 2950, 1390, 1260-1130, 1090(cm⁻¹)

15 Example 3

In a 300ml four-necked flask equipped with a magnetic stirrer, a thermometer, a reflux cooler, to which a trap was connected, and a nitrogen inlet tube, 50.2g (0.070mol) of N-n-propyl-N-[3-(trichlorosilyl)propyl]-perfluoroctylsulfonamide was placed, and 20 50ml of methanol was added thereto dropwise at 10-15°C over a period of 5 hours as nitrogen gas was vigorously being blown into the bottom of the flask. After the addition of the methanol was finished, the reaction mixture was further stirred for 5 hours. Thereafter, by removing the excess methanol by vacuum distillation, 38.2g (0.054mol) 25 of N-n-propyl-N-[3-(trimethoxysilyl)propyl]-perfluoroctylsulfonamide was obtained. Yield: 77%.

Example 4

In a 500ml three-necked flask equipped with a mechanical stirrer, a thermometer, a reflux cooler and a dropping funnel, 143.3g 30 (0.20mol) of pulverized N-n-propyl-N-[3-(trichlorosilyl)propyl]-perfluoroctylsulfonamide, 121.2g (1.2mol) of triethylamine was added and further 96g (3.0mol) of methanol was added dropwise over a period of 2 hours at 15-20°C under stirring as the flask was cooled by ice water.

35 After the addition of methanol, the produced salt was separated by filtration, 130.9g (0.186mol) of N-n-propyl-N-[3-(trimethoxysilyl)-propyl]-perfluorosulfonamide was obtained by vacuum distillation. Yield: 92.0%. B.P. 134°C/0.25mmHg.

Example 5

In a 300ml three-necked flask equipped with a mechanical stirrer, a reflux cooler and a dropping funnel, 71.7g (0.10mol) of N-n-propyl-N-[3-(trichlorosilyl)propyl]-perfluorooctylsulfonamide was placed and 75g of a 28% methanol solution of CH₃ONa was added dropwise at 15-20°C over a period of 2 hours.

After the addition of the methoxide, the produced salt was separated by filtration, 65.4g (0.093mol) of N-n-propyl-N-[3-(trimethoxysilyl)propyl]-perfluorooctylsulfonamide was obtained by vacuum distillation. Yield: 93.0%.

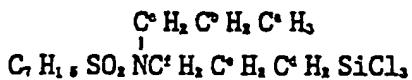
Example 6

In a 300ml four-necked flask equipped with a mechanical stirrer and a reflux cooler, 83.6g (0.10mol) of N-ethyl-N-[3-(tribromo-silyl)propyl]-perfluorooctylsulfonamide and 133.2g (0.9mol) of ethyl orthoformate were placed. To this mixture, 3.0g of aluminum chloride was added as a catalyst and the mixture was allowed to react at 80°C for 12 hours.

After the reaction was finished, 55.6g (0.076mol) of N-ethyl-N-[3-(triethoxysilyl)propyl]-perfluorooctylsulfonamide was obtained by vacuum distillation. Yield: 76.1%. B.P. 146°C/0.18mmHg.

Example 7

In a 100ml three-necked flask equipped with a magnetic stirrer, a thermometer and a reflux cooler, 53.1g (0.10mol) of N-n-propyl-perfluoroheptylsulfonamide, which was supplied by New Akita Chemical Co., and 10mg (1.9×10⁻⁵mol) of chloroplatinic acid were placed, and 14.9g (0.11mol) of trichlorosilane was added dropwise through a dropping funnel over a period of 1 hour at 60°C. After further stirring for 1 hour, the excess trichlorosilane was removed by distillation, and thus 61.3g of N-n-propyl-N-[3(trichlorosilyl)-propyl]-perfluoroheptylsulfonamide was obtained. Yield: 92%. The compound was confirmed to be:



by ¹HNMR analysis, MS analysis and IR spectrophotometric analysis.

Conditions and results of the analyses were as follows.

¹HNMR analysis:

Solvent: Flon-113, Internal standard: benzene
 δ 1.25(t, 3H, H-a), δ 1.6-2.5(m, 6H, H-b, d, e), δ 3.5-4.0(m,

4H, H-c, g), δ(s, 9H, H-d)

MS analysis:

Ionization voltage: 70eV

m/e, relative intensity and moiety are as follows in
this order: 504, 68.1%, M⁺-CH₂CH₂SiCl₃; 133, 21.1%,
·SiCl₃; 69, 100%, ·CF₃

IR photospectrometry:

Sample: neat

3350, 2950, 1390, 1260-1130(cm⁻¹)

10 Example 8

In a 500ml three-necked flask equipped with a magnetic stirrer, a thermometer and a reflux cooler, 133.3g (0.20mol) of N-n-propyl-N-[3-(trichlorosilyl)propyl]-perfluoroheptylsulfonamide, which was supplied by New Akita Chemical Co., was placed, and 200ml of methanol was added dropwise through a dropping funnel over a period of 5 hours at 35°C under a reduced pressure of 70mmHg. After the addition of methanol, 105.8g of N-n-propyl-N-[3(trimethoxysilyl)-propyl]-perfluoroheptylsulfonamide was obtained by vacuum distillation. Yield: 81%. The compound was confirmed to be:

20 C^cH₂C^cH₂C^cH₃

C₇H₁₅SO₂NC^cH₂C^cH₂Si(OCH^a₃),

by ¹HNMR analysis, MS analysis and IR spectrophotometric analysis.

Conditions and results of the analyses were as follows.

¹HNMR analysis:

25 Solvent: Flon-113, Internal standard: benzene

δ0.9(t, 2H, H-e), δ1.25(t, 3H, H-c), δ1.6-2.5(m, 6H, H-b, f)
δ3.5-4.0(m, 4H, H-c, g), δ3.8(s, 9H, H-d)

MS analysis:

Ionization voltage: 70eV

30 m/e, relative intensity and moiety are as follows in
this order: 622, 24.5%, M⁺-OCH₃; 504, 3.4%, M⁺-
·CH₂CH₂Si(OCH₃); 121, 100%, ·Si(OCH₃); 69, 100%, ·CF₃

IR spectrophotometry:

Sample: neat

35 3350, 2950, 1390, 1260-1130, 1090(cm⁻¹)

Example 9

In a 300ml three-necked flask equipped with a magnetic stirrer,

a thermometer and a reflux cooler, 73.4g (10.20mol) of N-ethyl-N-allyl-perfluorobutylsulfonamide and 5ml of 0.1M isopropanol solution of chloroplatinic acid (9.67×10^{-3} mmol) were placed, and 27.6g (0.24mol) of methyldichlorosilane was added dropwise at 60°C over a period of 1 hour. After the addition was finished, the stirring was further continued for 1 hour at the same temperature. The unreacted N-ethyl-N-allylperfluorobutylsulfonamide and methyldichlorosilane were distilled off and thus 73.1g of N-ethyl-N-[3-(dichloromethylsilyl)-propyl]-perfluorobutylsulfonamide was obtained. Yield: 76%. The compound was confirmed to be:



by ¹H NMR analysis, MS analysis and IR spectrophotometric analysis.

Conditions and results of the analyses were as follows.

15 ¹H NMR analysis:

Solvent: Flon-113, Internal standard: benzene
 δ 0.10(s, 3H), δ 1.30(t, 3H), δ 1.65-2.5(m, 4H), δ 3.5-4.0(m, 4H)

MS analysis:

20 Ionization voltage: 70eV

m/e and relative intensity are as follows:

339, 56.2%; 113, 24.6%; 69, 100%

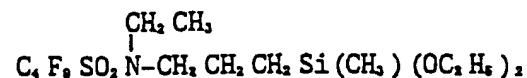
IR spectrophotometry:

Sample: neat

25 3350, 2950, 1390, 1260-1130(cm^{-1})

Example 10

In a 300ml three-necked flask equipped with a magnetic stirrer, a thermometer and a reflux cooler, 48.2g (0.10mol) of N-ethyl-N-[3-(dichloromethylsilyl)propyl]-perfluorobutylsulfonamide, 40.4g (0.40mol) of triethylamine and 150ml of isopropylether were placed and 30ml of ethanol was added dropwise over a period of 2 hours as the flask was being cooled by ice water. Thereafter, stirring was further continued for 1 hour at the same temperature. The produced salt was removed by filtration and the excess ethanol and isopropylether and triethylamine were distilled away and thus 38.6g of N-ethyl-N-[3-(diethoxymethylsilyl)propyl]-perfluorobutylsulfonamide was obtained. Yield: 77%. The compound was confirmed to be:



by ^1H NMR analysis, MS analysis and IR analysis.

Conditions and results of the analyses were as follows.

5 ^1H NMR analysis:

Solvent: Flon-113, Internal standard: benzene

δ 0.10(s, 3H), δ 1.31(t, 3H), δ 1.42(t, 6H), δ 1.6-2.5(m, 4H)
 δ 3.5-4.1(m, 8H)

MS analysis:

10 Ionization voltage: 70eV

m/e and relative intensity are as follows in this order:
370, 58.9%; 131, 100%; 69, 84.1%

IR spectrophotometry:

Sample: neat

15 3350, 2950, 1390, 1260-1130, 1090(cm^{-1})

Example 11

In a 200ml three-necked flask equipped with a magnetic stirrer, a thermometer and a reflux cooler, 18.9g (0.20mol) of N-ethyl-N-[3-(monoethoxydimethylsilyl)propyl]-amine, 15.8g (0.20mol) of pyridine and 100ml of isopropyl-ether were placed, and 30.2g (0.10mol) of perfluorobutylsulfonyl fluoride was added dropwise through a dropping funnel over a period of 1 hour at 20°C. The reaction mixture was stirred for 1 hour at that temperature and then further stirred for 2 hours at 40°C. Thereafter, the produced salt was removed by filtration, the excess pyridine and isopropylether were distilled off and 18.4g of N-ethyl-N-[3-(monoethoxydimethylsilyl)propyl]-perfluorobutylsulfonamide was obtained. Yield: 39%. The compound was confirmed to be:



30 by ^1H NMR analysis, MS analysis and IR spectrophotometric analysis.

Conditions and results of the analyses were as follows.

^1H NMR analysis:

Solvent: Flon-113, Internal standard: benzene

35 δ 0.1(s, 6H), δ 0.9(t, 2H), δ 1.3d(t, 3H), δ 1.6-2.5(m, 2H),
 δ 3.5-4.1(m, 4H), δ 3.8(s, 3H)

MS analysis:

Ionization voltage: 70eV

m/e and relative intensity are as follows:

426, 12.3%; 103, 62.2%; 69, 100%

IR spectrophotometry:

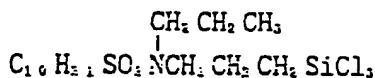
Sample: neat

5 3350, 2950, 1390, 1260-1130, 1090 (cm⁻¹)

Example 12

In a 50ml three-necked flask equipped with a magnetic stirrer, a thermometer and a reflux cooler, 20.4g (30mmol) of N-n-propyl-N-allylperfluorodecylsulfonamide, which was supplied by New Akita Chemical Co., and 5mg (1.0x10⁻⁴ mol) of chloroplatinic acid were placed, and 4.5g (33mmol) of trichlorosilane was added dropwise through a dropping funnel over a period of 20min at 80°C. Thereafter, the reaction system was stirred for 1 hour at the same temperature. By distilling off the excess trichlorosilane, 22.8g of N-n-propyl-N-[3-(trichlorosilyl)propyl]-perfluorodecylsulfonamide was obtained.

15 Yield: 93%. The compound was confirmed to be:



by ¹H NMR analysis, MS analysis and IR spectrophotometric analysis.

20 Conditions and results of the analyses were as follows.

¹H NMR analysis:

Solvent: Flon-113. Internal standard: benzene

δ1.31(t, 3H), δ1.7-2.6(m, 6H), δ3.6-4.1(m, 4H)

MS analysis:

25 Ionization voltage: 70eV

m/e and relative intensity are as follows in this order:

654, 72.3%; 133, 24.6%; 69, 100%

IR spectrophotometry:

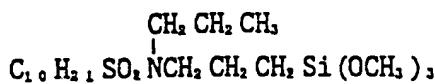
Sample: neat

30 3350, 2950, 1390, 1260-1130 (cm⁻¹)

Example 13

In a 100ml three-necked flask equipped with a magnetic stirrer, a thermometer and a reflux cooler, 16.3g (20mmol) of N-n-propyl-N-[3-(trichlorosilyl)propyl]-perfluorodecylsulfonamide was placed, and 20ml of methanol was added dropwise at 40°C under a reduced pressure of 60mmHg over a period of 1 hour. By distilling off the excess methanol, 12.1g of N-n-propyl-N-[3(trimethoxysilyl)propyl]-perfluorodecylsulfonamide was obtained. Yield: 75%. The compound

was confirmed to be:



by ^1H NMR analysis, MS analysis and IR spectrophotometric analysis.

5

Conditions and results of the analyses were as follows.

^1H NMR analysis:

Solvent: Flon-113, Internal standard: benzene
 δ 0.9(t, 2H), δ 1.24(t, 3H), δ 1.63-2.52(m, 6H), δ 3.4-3.9(m, 4H), δ 3.8(s, 9H)

10

MS analysis:

Ionization voltage: 70eV
 n/e and relative intensity are as follows in this order:
 772, 29.4%; 654, 5.6%; 121, 100%, 69, 89.1%

IR spectrophotometry:

15

Sample: neat
 3350, 2950, 1390, 1260-1130, 1090(cm^{-1})

The fluorine-containing silane compounds of the present invention have excellent water- and oil-repellency.

Example 14

20

An ordinary glass plate 24mmx75mm in dimension was immersed for 30sec. in a solution consisting of 1.0g of



and 100g of ethanol and 0.5g of a 10% HCl aqueous solution. The glass plate was dried at room temperature and the contact angle of the plate was measured. It was 110° for water and 75° for liquid paraffin.

Comparative Example 1

The procedures of Example 14 was repeated except that 1.0g of $\text{CH}_3\text{Si(OCH}_3)_3$, was used instead of said fluorine-containing silane compound. The contact angle was 35° for water and 37° for liquid paraffin.

Comparative Example 2

The procedures of Example 14 was repeated except that 1.0g of $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3$, was used instead of the fluorine-containing silane compound was used. The contact angle was 27° for water and 34° for liquid paraffin.

Example 15

A 25mmx75mm plate of ordinary glass was immersed in a solution

consisting of 1.0g of N-ethyl-N-[3-(triethoxysilyl)propyl]-perfluorohexylsulfonamide, 200ml of ethanol and 0.5g of a 10% hydrochloric acid for 1min and dried at room temperature.

The contact angle of the thus treated glass plate was 110° for
5 water and 76° for liquid paraffin.

Comparative Example 3

The procedures of Example 15 was repeated using 1.0g of trimethoxymethylsilane instead of the fluorine containing silane compound. The contact angle was 35° for water and 37° for liquid
10 paraffin.

Comparative Example 4

The procedures of Example 15 was repeated using 1.0g of 3-trimethoxysilylpropyl perfluoroheptylcarbonate instead of said fluorine containing silane compound. The contact angle was 81° for
15 water and 49° for liquid paraffin.

Example 16

Three grams of N-n-propyl-N-[3-(trimethoxysilyl)propyl]-perfluorobutylsulfonamide was admixed with 100g of epoxy resin paint base (melamine-hardenable epoxy resin supplied by Tokyo Paint
20 Kabushiki Kaisha) and the mixture was applied to 50mmx100mmx1mm steel test panel (marketed by Nippon Test Panel Kabushiki Kaisha) to a thickness of 0.1mm and cured at 120°C for 20min. The contact angle of the surface was measured as indices of water-repellency and oil-repellency. The angle was 112° for water and 85° for liquid paraffin.

Comparative Example 5

The epoxy resin used in Example 16 was applied to 50mmx100mmx1mm steel test panel (marketed by Nippon Test Panel Kabushiki Kaisha) to a thickness of 0.1mm without addition of the fluorine-containing silane compound and cured at 120°C for 20min. The test for water- and oil-repellency was carried out in the same manner as in Example 16. The contact angle was 33° for water and 12° for liquid paraffin.

Comparative Example 6

The procedures of Example 16 was repeated using 3g of 2-trifluoromethyl-1-trimethoxysilylethane. The contact angle was 45° for water and 23° for liquid paraffin.

When inorganic fillers such as glass fiber, glass beads, alumina, graphite, carbon fiber, molybdenum disulfide, metal powders

such as bronze powder, lead powder, etc. are treated with the fluorine-containing silane compound of the present invention, they can be easily mixed with fluorine resins such as polytetrafluoroethylene, polychlorotrifluoroethylene, poly(vinylidene fluoride), poly(vinyl fluoride), hexafluoroethylene-hexafluoropropene copolymer, tetrafluoroethylene-ethylene copolymer, tetrafluoroethylene-perfluoroalkylvinylether copolymer, chlorotrifluoroethylene-ethylene copolymer, etc. with good affinity and the resulting resin composition has excellent compression resistance and abrasion resistance.

Usually, 0.1-20% by weight of the fluorine-containing silane compound is used on the basis of the weight of fillers.

Example 17

Fifty (50) grams of glass fiber (about 3 μ m in diameter and about 50 μ m in length) was immersed in 500ml of an ethanol solution of 2.5g of

$C_8F_{17}SO_2N(C_2H_5)_2CH_2CH_2Si(OCH_3)_2$, containing 1 % by weight of a 10% HCl aqueous solution and the mixture was vigorously agitated by means of an electric shaker for 10min at room temperature. The glass fiber thus treated with the fluorine-containing silane compound was mixed with polytetrafluoroethylene (Teflon[®]) powder at a weight ratio of 50:50 and the mixture was compacted by a pressure of 400kg/cm² to a piece 172mm in diameter and 10mm in thickness. The piece was baked at 370°C for 1 hour and a glass-fiber-reinforced Teflon[®] resin was obtained.

The compression strength (compression rate 3mm/min) and friction properties and abrasion properties were measured. The compression strength was measured at a compression rate of 3mm/min, the friction and abrasion properties were measured using a Suzuki's abrasion tester. The results are shown in Table 1 together with the results of the following comparative example.

Comparative Example 7

The procedures of Example 17 were repeated using the same glass fiber which was not treated with said fluorine-containing silane compound, and thus a glass-fiber-reinforced Teflon[®] resin piece was obtained and the tests were carried out with this resin piece. The results are shown in Table 1.

Table 1

		<u>Example 17</u>	<u>Comp. Ex. 7</u>
Compression strength			
5	Load required for 1% deformation (kg/cm ²)	98	84
	" " 25% "	346	305
	Friction coefficient* static	0.07	0.07
	dynamic	0.24	0.24
	Abrasion coefficient* (kg/cm ²)	1.1x10 ⁻⁵	1.1x10 ⁻⁵
10	*Test conditions: Counter piece: SUS27 stainless steel piece, 256mmx20mmx15mm		
	Load: 4kg/cm ²		
	Rate: 60m/min		
15	Time: 16hrs after 30min of pre-operation		

Example 18

In a 1 liter three-necked flask equipped with a thermometer, a stirrer and a reflux cooler, 50g of graphite powder was placed and 20 100ml of a 10% by weight of solution of the same fluorine-containing silane compound as used in Example 17 was added dropwise over a period of 1 hour under stirring. Thereafter, the mixture was heated to 100°C to remove the solvent. The thus obtained treated graphite powder was mixed with the same Teflon® resin and the same tests were 25 carried out. The results are shown in Table 2.

Comparative Example 8

The procedures and tests of Example 17 were repeated with untreated graphite powder and the results are shown in Table 2.

30 Table 2Example 18 Comp. Ex. 8**Compression strength**

	Load required for 1% deformation (kg/cm ²)	85	76
	" " 25% "	391	355
35	Friction coefficient* static	0.05	0.06
	dynamic	0.23	0.23
	Abrasion coefficient* (kg/cm ²)	6.7x10 ⁻⁶	6.7x10 ⁻⁶

When inorganic fillers such as silicon oxide, tin oxide, titanium oxide, aluminum oxide, silicon nitride, graphite, zinc oxide, iron oxides, mica, glass fiber, carbon fiber, asbestos, etc. are treated with the fluorine-containing silane compound of the present invention, they are provided with excellent water- and oil-repellency and non-tackiness.

5 Usually, 0.1-20% by weight of the fluorine-containing silane compound is used on the basis of the weight of the filler.

Example 19

10 Fifty (50) grams of silica powder (about 1 μm in diameter) was mixed with 500ml of ethanol solutions respectively containing 0.1, 1, 5 and 10% by weight of

15 $\text{C}_6\text{F}_{11}\text{SO}_3\text{N}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$, on the basis of the weight of the filler and 1% by weight of a 10% HCl aqueous solution. and the mixture was vigorously agitated by means of an electric shaker for 10min at room temperature.

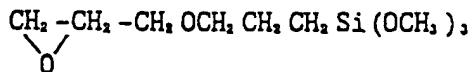
20 The mixture was heated to 100°C to remove the solvent by evaporation and thus silica powders treated with the fluorine-containing silane compound were obtained. Substantially all of the added fluorine-containing silane compound adhered to the silica powder.

25 The IR absorption spectra of the thus treated silica powders were measured by powder reflection method and it was observed that there were an absorption caused by the C-H bond at 2850-2950cm $^{-1}$, an absorption caused by the sulfonamide bond at 1390cm $^{-1}$ and an absorption caused by the C-F bond at 1100-1300cm $^{-1}$. That is, it was revealed that the fluorine-containing silane compound exists on the surface of the silica powders.

30 The water repellency of the thus treated silica powders were measured. The powders were respectively mixed with 500ml of water and vigorously agitated with an electric shaker for 15 minutes at room temperature. The water repellency was evaluated based on the observation by the naked eye.

Comparative Example 9

35 The procedures of Example 19 was repeated using



The results are summarised in Table 3 together with those of Example

19.

Table 3

5	<u>Example 19</u>		<u>Comparative Example 9</u>	
	F-containing silane compound content (% by weight)	Water repellency	Silane compound content (% by weight)	Water repellency
10	0.1	O	1	X
	1	O		
	5	O	10	X
	10	O		

x: Silica powder completely disperses in water.

15 O: Silica powder partly disperses in water and partly floats on the water surface.
◎: Silica powder completely floats on the water surface.

Example 20

20 In a 1 liter three-necked flask equipped with a thermometer, a stirrer and a reflux cooler, 50g of alumina powder (about 1μm in diameter) was placed and 50ml of solutions (5, 10, 20 and 25% by weight) of the same fluorine-containing silane compound were respectively added dropwise over a period of 1 hour under stirring. Thereafter each mixture was heated to 100°C to remove the solvent. Thus alumina powders treated with the same fluorine-containing silane compound were obtained.

25 It was confirmed that the fluorine-containing silane compound adhered to the surface of alumina powder with the IR absorption spectra by the powder reflection method in the same manner as in Example 19.

Comparative Example 10

30 The procedures and tests of Example 19 were repeated using $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$, as a silane compound. The results are shown in Table 4 together with those of Example 19.

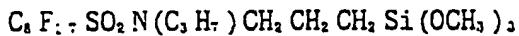
Table 4

	<u>Example 19</u>		<u>Comparative Example 10</u>	
	F-containing silane compound content (% by weight)	Water repellency	Silane compound content (% by weight)	Water repellency
5	5	O	5	X
10	10	O		
15	20	O	20	O
20	25	O		
25				
30				

Symbols have the same meanings as in Table 3

Example 21

15 Fifty (50) grams of silica powder (about $10\mu\text{m}$ in diameter) was mixed with 500ml of ethanol solutions respectively containing 0.1, 1, 5 and 10% by weight of



20 on the basis of the weight of the filler and 1% by weight of a 10% HCl aqueous solution and the mixture was vigorously agitated by means of an electric shaker for 20min at room temperature.

The mixture was heated to 100°C to remove ethanol by evaporation and thus silica powders treated with said fluorine-containing silane compound was obtained. The IR absorption spectra of the thus treated silica powders were measured by the powder reflection method and it was observed that there were an absorption caused by the C-H bond at $2850\text{-}2950\text{cm}^{-1}$, an absorption caused by the SO_2N bond at 1390cm^{-1} and an absorption caused by the C-F bond at $1100\text{-}1300\text{cm}^{-1}$. That is, it was confirmed that the fluorine-containing silane compound exists on the surface of the silica powders.

30 The thus treated silica powders were respectively mixed with an epoxy resin paint base (melamine-hardenable epoxy resin supplied by Tokyo Paint Kabushiki Kaisha) in an amount of 50% by weight of the resin paint base and the mixture was applied on the surface of steel test panels to a thickness of $100\mu\text{m}$. The coated test panels were 35 cured at 140°C for 20min and tested for water resistance. That is, the panels were heated in an autoclave containing water under a pressure of 5atm for 2 hours. Thereafter, the water content of the

coating was measured. The results are shown in Table 5.

Comparative Example 10

The procedures of Example 21 were repeated using
 $\text{CH}_3\text{Si}(\text{OCH}_3)_3$.

5 The results are shown in Table 5.

Table 5

<u>Example 21</u>		<u>Comparative Example 10</u>	
	F-containing silane compound content (% by weight)	Silane compound content (% by weight)	Water content
10	0.1	≤0.3%	1
	1	≤0.2%	≥3%
15	5	≤0.2%	10
	10	≤0.2%	≥2%

Example 22

In a 1 liter three-necked flask equipped with a thermometer, a stirrer and a reflux cooler, 50g of alumina powder (about $10\mu\text{m}$ in diameter) was placed and 50ml of solutions (5, 10, 20 and 25% by weight) of the same fluorine-containing silane compound as that used in Example 21 was added dropwise over a period of 1 hour under stirring. Thereafter the mixture was heated to 100°C to remove the solvent. With respect to the thus treated silica powders, the presence of the fluorine-containing silane compound on the surface thereof was confirmed by the IR absorption spectra by the powder reflection method in the same manner as in Example 21. Further the same water resistance test as that carried out in Example 21 was conducted. The results are shown in Table 6.

Comparative Example 11

The procedures and tests of Example 22 were repeated using $\text{CH}_3\text{Si}(\text{OCH}_3)_3$, which was used in Comparative Example 10 as a silane compound. The results are shown in Table 6 for comparison with those of Example 22.

Table 6

<u>Example 22</u>		<u>Comparative Example 11</u>	
	F-containing silane compound content (% by weight)	Water content	Silane compound content (% by weight)
5	5	≤0. 2%	5
	10	≤0. 2%	
	20	≤0. 2%	20
10	25	*	≥2%

* Poor dispersion. No coating material formed.

15 Example 23

The procedures of Example 22 was repeated using alumina powder (about $5\mu\text{m}$ in diameter). The results are shown in Table 7.

Comparative Example 12

20 The procedures of Example 23 was repeated using
 $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_2$,
as a silane compound. The results are shown in Table 7 for the
comparison with Example 23.

Table 7

<u>Example 23</u>		<u>Comparative Example 12</u>	
	F-containing silane compound content (% by weight)	Water content	Silane compound content (% by weight)
30	0. 1	≤0. 2%	1
	1	≤0. 1%	
	5	≤0. 1%	10
	10	≤0. 1%	≥1%

35 Example 24

The procedures of Example 22 was repeated using 50g of alumina powder (not larger than about $5\mu\text{m}$ in diameter). The results are shown in Table 8.

Comparative Example 13

The procedures of Example 22 was repeated using
 $\text{NH}_2(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$,
as a silane compound. The results are shown in Table 8 for the
5 comparison with those of Example 24.

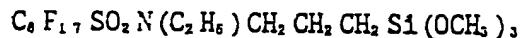
Table 8

	<u>Example 24</u>	<u>Comparative Example 13</u>
	F-containing silane compound content (% by weight)	Silane compound content (% by weight)
10	5 $\leq 0.2\%$	5 $\geq 1\%$
	10 $\leq 0.1\%$	
15	20 $\leq 0.1\%$	10 $\geq 1\%$
	25 *	

* Poor dispersion. No coating composition formed.

Example 25

20 Fifty (50) grams of glass fiber (about $3\mu\text{m}$ in diameter and about $50\mu\text{m}$ in average length) was mixed with 500ml of acetone solutions containing various amounts of



25 containing 1% by weight of a 10% HCl aqueous solution, and the mixture was stirred for 20min at room temperature. The concentrations of the fluorine-containing silane compound in these solutions were 0.1, 1, 5 and 10% by weight on the basis of the weight of glass fiber. After 30min, acetone was removed by heating to 100°C and the thus treated glass fibers were tested for the IR spectrum by the diffusion reflection method. Absorptions were observed at $2859-2950\text{cm}^{-1}$ (C-H), 1390cm^{-1} (SO₂N) and $1100-1300\text{cm}^{-1}$ (C-F) and thus it was confirmed that the fluorine-containing silane compound was present on the surface of glass fiber. The thus treated glass fiber was mixed 30 with an acryl resin paint base (self-curable acryl resin paint base supplied by Tokyo Paint Kabushiki Kaisha) in an amount of 50% by weight and the mixture was poured into a $10\text{cm} \times 10\text{cm} \times 10\text{cm}$ mold and 35 cured at 150°C for 30min. The thus obtained acryl resin lump was

subjected to a water resistance test with steam at 5atm for 2 hours in the same manner as in Example 21. The water content was measured and the results are shown in Table 9.

Comparative Example 14

5 The procedures of Example 25 was repeated using $\text{CH}_3\text{Si}(\text{OCH}_3)_3$, as a silane compound and the results are shown in Table 9.

Table 9

	<u>Example 25</u>		<u>Comparative Example 14</u>	
	F-containing silane compound content (% by weight)	Water content (% by weight)	Silane compound content (% by weight)	Water content ≥5%
10	0.1	≤0.8%	1	≥5%
15	1	≤0.5%		
	5	≤0.5%	10	≥3%
	10	≤0.5%		

20 When metallic materials such as copper, aluminum, iron, lead, zinc, tin, titanium, cobalt, nickel, chromium, etc.; alloys such as stainless steels, Hastelloy®, Inconel®, Stellite®, etc.; magnetic alloys such as Sm-Co alloy, Nd-Fe-B alloy, etc. are treated with the fluorine-containing silane compound of the present invention, they 25 are provided with excellent water- and oil-repellency. The metallic materials can be in the forms of sheet, sphere, ribbon, etc.

Also, when organic resin materials such as phenol resin, furane resin, xylene-formaldehyde resin, ketone-formaldehyde resin, urea resin, melamine resin, aniline resin, epoxy resin, poly(vinyl acetate) resin, polyacryl resin, polymethacryl resin, poly(vinyl chloride) resin, poly(vinylidene chloride) resin, polyacrylonitrile resin, polyvinylether resin, polycarbonate resin, polyamide resin, polyurethane resin, etc. including almost all hydrocarbon resins are 30 treated with the fluorine-containing silane compound of this invention, they are provided with excellent water- and oil-repellency. The resin materials can be in the form of sheet, film, fiber or in any other form. Adherence and effect of the compounds of 35 the present invention are not influenced by the shape of the

substrate materials.

Also, when paper is treated with the fluorine-containing silane compound of the present invention, such paper is provided with excellent water- and oil-repellency. The paper encompasses machine-made paper, hand-made paper, cardboard, corrugated cardboard, etc.

The fluorine-containing silane compound of the present invention is applicable to glass to provide it with excellent water- and oil-repellency.

The fluorine-containing silane compound of the present invention can be added to paper-making pulp slurry when incorporation in paper is intended.

The fluorine-containing silane compound of the present invention can be applied to the surface of various materials by admixing with a resin coating composition.

Example 26

A 0.5% acetone solution of



containing 0.5% by weight of a 10% acetic acid aqueous solution was applied to a 100mmx50mmx1mm aluminum plate.

The contact angles of this plate for water and liquid paraffin were measured for evaluation of its water- and oil-repellency. The results are shown in Table 10.

Comparative Examples 15

The same aluminum plate as used in Example 26 was coated with an acryl resin paint base (a self-curing type acryl resin supplied by Tokyo Paint Kabushiki Kaisha) to the coating weight of 3% by weight.

Water- and oil-repellency of this aluminum plate were measured and the results are shown in Table 10 together with the results of Example 26.

30

Table 10

	<u>Contact Angle (°)</u>	
	<u>Water</u>	<u>Liquid paraffin</u>
35	Example 26	143°
	Comp. Ex. 15	96°
		28°

Example 27

A 5% acetone solution of
 $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$,
 containing 1% by weight of a 10% HCl aqueous solution was applied to
 a 100mmx50mmx1mm copper plate.

5 The plate was dried at 80°C for 1 hour. The coated copper plate
 was checked by IR spectrophotometry and there was observed absorption
 of the C-F bond at 1100-1300cm⁻¹. That is, adhesion of the fluorine-
 containing silane compound was confirmed.

10 The plate was immersed in a 5% common salt aqueous solution and
 weight loss was measured.

Comparative Example 16

15 The same copper plate as used in Example 27 which was not
 treated with the fluorine-containing silane compound was tested in
 the same manner. The results of Example 27 and Comparative Example
 16 are shown in Table 11.

Table 11

	<u>No. of days</u>	<u>Example 27</u>	<u>Comp. Ex. 16</u>
20	1	0%	5%
	2	1%	8%
	3	3%	12%
	5	5%	18%
	10	8%	24%

25

Example 28

30 A 5% by weight ethanol solution of
 $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$,
 containing 0.5% by weight of a 10% n-propylamine aqueous solution was
 applied to a 100mmx50mmx1mm steel plate.

The plate was allowed to stand outdoors and staining of this
 surface was observed.

Comparative Example 17

35 The procedures of Example 28 were repeated using untreated steel
 plated. The results are shown in Table 12.

Table 12

<u>No. of days</u>	<u>Example 28</u>	<u>Comp. Ex. 17</u>
1	O	O
5	O	Δ
10	O	X
30	O	X
60	O	X
100	Δ	X

10 O: Clean (no stain)

Δ: Stains in several places

X: Stained overall

Example 29

15 Five (5) grams of



was added to 100g of an epoxy resin paint base (melamine-hardenable epoxy resin supplied by Tokyo Paint Kabushiki Kaisha). The paint was applied to a 100mmx50mmx1mm test panel (marketed by Nippon Test Panel Kabushiki Kaisha) to a thickness of 0.1mm and the panel was baked at 120°C for 20min. Contact angles for water and oil were measured for evaluation of water- and oil-repellency.

Comparative Example 18

Using the epoxy resin paint base used in Example 29 containing no fluorine-containing silane compound, a test panel was prepared and tested in the same manner as in Example 29. The results are shown in Table 13.

Table 13

30

	<u>Contact Angle (°)</u>	
	<u>Water</u>	<u>Liquid paraffin</u>
Example 29	106°	78°
Comp. Ex. 18	72°	18°

35

Example 30

The epoxy resin paint base used in Example 29 was applied to a 100mmx50mmx1mm test panel (marketed by Nippon Test Panel Kabushiki

Kaisha) to a thickness of 0.1mm and the panel was pre-baked at 80°C for 30min.

This panel was immersed in a 10% by weight Flon-113 solution of $C_8F_{17}SO_2N(C_2H_5)CH_2CH_2CH_2Si(OCH_3)_3$, 5 for 10sec and baked at 120°C for 20min. The thus treated panel was checked by IR spectrophotometry and there was observed absorption of the C-F bond at $1100-1300\text{cm}^{-1}$. Water- and oil-repellency of this panel was checked in the same manner.

Comparative Example 19

10 The procedures of Example 30 was repeated using a fluorine-containing surfactant $C_8F_{17}SO_2Na$. Water- and oil-repellency were evaluated in the same manner.

Table 14

	Contact Angle (°)	
	Water	Liquid paraffin
Example 30	110°	82°
Comp. Ex. 19	74°	20°

20

Example 31

An acryl resin paint base (self-curing acryl resin marketed by Tokyo Paint Kabushiki Kaisha) was applied to a 100mmx50mmx1mm test panel (supplied by Nippon Test Panel Kabushiki Kaisha) to a thickness of 0.1mm and the panel was baked at 170°C for 20min.

This panel was immersed in a 10% by weight acetone solution of $C_8F_{17}SO_2N(C_2H_5)CH_2CH_2CH_2Si(OCH_3)_3$, 25 for 30sec and dried at room temperature. The thus treated panel was checked by IR spectrophotometry and there was observed an absorption of the C-F bond at $1100-1300\text{cm}^{-1}$. Adhesion of the fluorine-containing silane compound was confirmed.

Comparative Example 20

The procedures of Example 31 was repeated using a fluorine-containing surfactant $C_8F_{17}CO_2K$ instead of said fluorine-containing silane compound. No C-F bond was recognized by IR spectrophotometry.

Water- and oil-repellency were evaluated in the same manner. The results are shown in Table 15.

Table 15

		Contact Angle (°)	
		Water	Liquid paraffin
5	Example 31	105°	80°
	Comp. Ex. 20	72°	28°

Example 32

Commercially available A4 size letter paper (marketed by Kokuyo Kabushiki Kaisha) was immersed in a 3% by weight acetone solution of $C_2F_5SO_2N(C_2H_5)_2CH_2CH_2CH_2Si(OCH_3)_2$, for 5min and dried at room temperature for 2 hours. Thus paper impregnated with said fluorine-containing silane compound was obtained. The paper was checked by IR spectrophotometry and there was observed absorption of the C-F bond at $1100-1300\text{cm}^{-1}$. Adhesion of the fluorine-containing silane compound was confirmed.

Water and liquid paraffin were dropped on this paper and the absorption was observed and evaluated.

Comparative Example 21

The procedures of Example 32 was repeated with respect to the same but untreated paper. The results of Example 32 and Comparative Example 21 are shown in Table 16.

Table 16

		Absorption time	
		Water	Liquid paraffin
	Example 32	42sec	1min 12sec
30	Comp. Ex. 21	within 1sec	within 5sec

Example 33

On the basis of the weight of pulp, 2% of $C_2F_5SO_2N(C_2H_5)_2CH_2CH_2CH_2Si(OCH_3)_2$, was added to a pulp slurry and paper was made.

In IR spectrophotometry, absorption of the C-F bond was observed at $1100-1300\text{cm}^{-1}$.

In the same manner as in Example 32, water- and oil-repellency were evaluated.

Comparative Example 22

The procedures of Example 33 was repeated without using the fluorine-containing silane compound. The results of Example 33 and Comparative Example 22 were shown in Table 17.

5

Table 17

		Absorption time	
		Water	Liquid paraffin
10	Example 33	1min 7sec	1min 59sec
	Comp. Ex. 22	less than 1sec	within 5sec

Example 34

Commercially available corrugated cardboard (marketed by Kashiwaya Shiki Kogyo Kabushiki Kaisha) was immersed in a 5% by weight benzene solution of

$C_6F_{11}SO_2N(C_2H_5)CH_2CH_2CH_2Si(OCH_3)_3$,
for 3min and dried at 50°C for 1 hour.

Said cardboard was checked by IR spectrophotometry and absorption due to the C-F bond was observed at 1100-1300cm⁻¹. That is, presence of the fluorine-containing compound was confirmed.

Water- and oil- repellency of the cardboard was evaluated in the same manner.

Comparative Example 23

The procedures of Example 34 was repeated using $C_6F_{11}SO_2N(C_2H_5)CH_2CH_2PO(ONa)_2$, instead of said fluorine-containing silane compound. The results of Example 34 and Comparative Example 23 are shown in Table 18.

30

Table 18

		Absorption time	
		Water	Liquid paraffin
	Example 34	1min 16sec	1min 39sec
35	Comp. Ex. 23	47sec	1min 3sec

When colored ceramic materials such as tiles, pottery and porcelain wares, etc. are treated with the fluorine-containing silane

compound of the present invention, they are provided with excellent color-fastness and increased chemical resistance. Leaching of pigments or pigment elements (cadmium, lead, etc. for instance) is well prevented. In the case of tiles, growth of molds and mosses on the surface is prevented.

Example 35

Colored tiles were prepared by coating commercially available colorless semi-porcelain tiles with a paste made by mixing 5 parts by weight of cadmium pigment, 95 parts by weight of non-lead boric acid low temperature glaze (SK010a), 0.2 part by weight of methyl cellulose and 60 parts by weight water and ball-milling the mixture for 30min and firing the coated tiles at 1000°C after drying.

The thus prepared colored tiles were coated with N-n-propyl-N-[3-(trimethoxy)silylpropyl]-perfluorooctylsulfonamide diluted with ethanol to the concentration indicated in Table 19 and dried. Each of the thus treated tiles was soaked in 300ml of a 4% acetic acid solution for 24 hours. Thereafter, the amount of cadmium leached out was measured by atomic absorption spectrometer. Also the tiles were dried and checked for deposition of alkali on the surface (efflorescence). The results are summarized in Table 19.

Examples 36

Colored tiles were prepared by coating commercially available colorless semi-porcelain tiles with a paste made by mixing 0.68 part by weight of ferric oxide, 0.32 part by weight of cobalt oxide, 100 parts by weight of non-lead low temperature glaze (SK010a), 0.2 part by weight of methyl cellulose and 60part by weight of water and ball-milling the mixture for 30min and firing the coated tiles at 1050°C after drying.

The thus prepared colored tiles were coated with N-n-propyl-N-[3-(trichloro)silylpropyl]-perfluorooctylsulfonamide diluted with ethanol to the concentration indicated in Table 19 and dried. Each of the thus treated tiles was soaked in 300ml of a 4% acetic acid solution for 24 hours. Thereafter, the amount of lead leached out was measured by an atomic absorption spectrometer. Also the tiles were dried and checked for deposition of alkali on the surface. The results are shown in Table 19.

Example 37

Colored tiles were prepared by coating commercially available

colorless semi-porcelain tiles with a paste made by mixing 2 parts by weight of manganese oxide, 98 parts by weight of non-lead medium temperature glaze (SK4), 0.2 part by weight of methyl cellulose and 60 parts by weight of water and ball-milling the mixture for 30min and firing the coated tiles at 1200°C after drying.

The thus prepared colored tiles were coated with N-n-propyl-N-[3-(trichloro)silylpropyl]-perfluoroctylsulfonamide diluted with ethanol to 5% in concentration. The thus treated tiles were immersed in water to the middle thereof and allowed to stand for observing growth of molds and mosses. After 3 months, growth of molds and mosses was not observed.

Comparative Example 24

The colored tiles prepared in Example 35 were immersed in a 4% acetic acid solution for 24 hours without surface treatment and leaching of cadmium was measured by atomic absorption spectrometry. Also deposition of alkali was checked.

Comparative Example 25

The colored tiles prepared in Example 36 were checked for leaching of lead and deposition of alkali in the same manner as in Comparative Example 24. The results are shown in Table 19.

Table 19

	Ex.	Sample	Conc. %	Leaching (ppm)		Deposition of Alkali (Visual Observation)	
				Cd	Pb		
25	Ex. -	35	1	1.0	0.05	-	None
		35	2	5.0	0.00	-	"
		35	3	10.0	0.00	-	"
30	Comp. Ex. 24		-	15	-	Recognized	
	Ex. 36	1	1.0	-	0.08	None	
		36	2	5.0	-	0.00	
		36	3	10.0	-	0.00	
35	Comp. Ex. 25		-	-	58.6	Recognized	

Example 38

Colored tiles were prepared by coating commercially available colorless semi-porcelain tiles with a paste made by mixing 2 parts by

weight of manganese oxide, 92 parts by weight of non-lead medium temperature glaze (SK4), 0.2 part by weight of methyl cellulose and 60 parts by weight of water and ball-milling the mixture for 30min and firing the coated tiles at 1200°C after drying.

5 The thus prepared colored tiles were coated with N-n-propyl-N-[3-(trichloro)silylpropyl]-perfluorooctylsulfonamide diluted with ethanol to 5% in concentration. The thus treated tiles were immersed in water to the middle thereof and allowed to stand for observing growth of molds and mosses. After 3 months, growth of molds and
10 mosses was not observed.

Comparative Example 26

The colored tiles prepared in Example 37 were checked for growth of mold and mosses without treating surface treatment in the same manner in as in Example 37. Mosses grew within 1 month.

15 When inorganic construction materials such as masonry joint materials, ALC (air-entrained light concrete) plates, slate boards, calcium silicate boards, shaped cement materials, cured cement mortar, concrete, etc. are treated with the fluorine-containing silane compound of the present invention, they are provided with
20 improved water-repellency, oil-repellency, stain resistance, weathering resistance, good adhesion of coating materials, etc. and further provided with resistances to freezing, growth of molds and mosses, etc. These construction materials can be coated with some other coating material before treated with the fluorine-containing
25 silane compound of the present invention.

When these materials are treated with the fluorine-containing silane compound of the present invention, the compound is usually diluted with a suitable organic solvent in a concentration of 0.001-20%, preferably 0.1-10% by weight.

30 Example 39

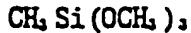
A masonry joint material was prepared by mixing 100 parts by weight of portland cement, 300 part by weight of sand, 0.2 part by weight of methyl cellulose and 60 parts by weight of water. This material was applied to a 30cmx30cmx5cm concrete block to the thickness of 5mm by a trowel. After the material spread on the block was cured in moist air for 2 weeks, a 5% ethanol solution of
35 C₆F₁₃SO₂N(CH₃)CH₂CH₂CH₂Si(OCH₃)₃,

was applied on the material and dried. This test block was immersed

in water to 5cm from the base and allowed to stand in a room of 35°C and 95%RH for 3 months. No growth of molds and mosses was observed.

Comparative Example 27

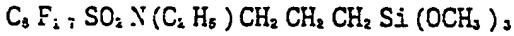
On the surface of the test block prepared in Example 39, 5% ethanol solution of



was applied and the block was tested in the same manner as in Example 39. Molds grew in 3 months.

Example 40

An emulsion paint was prepared by mixing 40 parts by weight of an acrylic emulsion coating material ("EC720" marketed by Dai-Nippon Ink Kogyo Kabushiki Kaisha), 25 parts by weight of titanium oxide, 0.2 parts by weight of sodium oleate and 0.3 part by weight of methyl cellulose. This paint was applied on the surface of a 150x50x3mm slate board. After the paint was dried, a 0.1% ethanol solution of



was applied on the painted surface of the slate board once.

The edges and back side of this test plate were protected and the plate was subjected to an outdoor exposure test for 1 year.

After 1 year, blistering, peeling-off and stain of the paint on the surface were not observed.

Comparative Example 28

On the painted surface of the test slate plate prepared in Example 40, a 5% ethanol solution of



was applied and dried. The plate was subjected to the outdoor exposure test for 1 year in the same manner as in Example 40.

Although blistering and peeling-off did not occur, the surface was remarkably stained.

Comparative Example 29

On the painted surface of the test slate plate prepared in Example 40, a 5% ethanol solution of known



was applied and dried. The plate was subjected to the outdoor exposure test for 1 year in the same manner as in Example 40.

Although blistering and peeling-off did not occur, the surface was slightly stained.

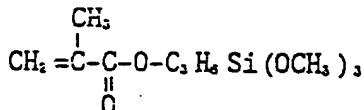
Example 41

A silica paint was prepared by mixing 20 parts by weight of a colloidal silica ("Snow Tex" marketed by Nissan Kagaku Kabushiki Kaisha), 10 parts by weight of titanium oxide, 20 parts by weight of calcium carbonate, 0.2 part by weight of sodium oleate, 0.4 part by weight of methyl cellulose and 50 parts by weight of water. This silica paint was applied on the surface of a 150mmx50mmx3mm slate board. After the paint was dried, a 5% ethanol solution of $C_8F_{17}SO_2N(CH_3)_2CH_2CH_2Si(OCH_3)_3$, was applied on the painted surface of the slate board once.

The edges and back side of this test plate were protected and the lower half of the plate was immersed in water. After 3 months, blistering and peeling-off did not occur and almost no stain was observed at the water level line.

Comparative Example 30

On the surface of the slate board coated with the silica paint prepared in Example 41, a 5% ethanol solution of



was applied and dried. The lower half of the slate board was immersed in water. After 3 months, the paint layer peeled off in the vicinity of the water level line.

Example 42

A 150mmx40mmx40mm ALC block was soaked in a 10% ethanol solution of

$C_8F_{17}SO_2N(CH_3)_2CH_2CH_2CH_2Si(OCH_3)_3$, for impregnation and dried. The test block was wholly immersed in water and subjected to a cycle test of freezing and thawing comprising chilling to -20°C for 2 hours and keeping at 30°C for 2 hours. Two cycles were conducted per day. After 50 cycles, cracking and breaking did not occur.

Comparative Example 31

The same ALC block used in Example 42 was soaked in a 10% ethanol solution of

$C_8F_{17}CH_2CH_2CH_2Si(OCH_3)_3$, for impregnation and dried and subjected to the same test as in Example 42. Although no cracking and breaking occurred after 20 cycles of freezing and thawing, cracking occurred at 40 cycles and

the block broke at 50 cycles.

Comparative Example 32

The same ALC block used in Example 42 was soaked in a 10% ethanol solution of

5 $C_8H_7Si(OCH_3)_3$,

for impregnation and dried and subjected to the same test as in Example 42. The block chipped after 20 cycles of freezing and thawing and broke after 30 cycles.

Example 43

10 On the surface of a 300mmx300mmx5mm slate board, a 10% ethanol solution of

$C_8F_17SO_2N(C_8H_7)CH_2CH_2CH_2SiCl_3$,

were applied once and dried. Water permeability of this slate board was tested in accordance with the method of JIS A6910. Even 15 after 24 hours, no absorption of water was recognized.

Comparative Example 33

The same slate board as used in Example 43 was subjected to the test of Example 43 without being treated with the fluorine-containing silane compound. After 1 hour, water in excess of 30ml was absorbed.

20 Example 44

A cement block was made by mixing 100 parts by weight of portland cement, 200 parts by weight of sand and 40 parts by weight of water and moulding. The block was cured for 1 day at room temperature. A 5% ethanol solution of

25 $C_8F_17SO_2N(CH_3)CH_2CH_2CH_2Si(OCH_3)_3$,

was applied on the surface of the block and dried. The side and back surfaces were protected and the block was allowed to stand under the conditions of 5°C and 95% humidity. No deposition of alkali occurred even after 1 month.

30 Comparative Example 34

The cement block made in Example 44 was subjected to the same test without being treated with the fluorine-containing silane compound. After 1 week, deposition of alkali on the surface occurred.

When the surface of metals such as copper, a typical 35 electroconductive material, gold, silver, iron, aluminum and various kinds of alloys is treated with the fluorine-containing silane compound of the present invention, it repels molten solder and soldering paste and loses solderability. That is, the treated

surface becomes unsolderable. Solderability can be easily regained by removing, by scraping for instance, the fluorine-containing silane compound layer and thus the treated metal sheet will be used for manufacturing integrated circuits.

5 Example 45

A 0.5% ethanol solution of



containing 0.3% by weight of a 10% sulfuric acid solution was applied to a 100x50x1mm copper plate. On the surface of this treated copper 10 plate, molten tin-lead solder was dropped. After cooled, the solder drop did not adhere to the copper plate and readily removed when lightly touched upon.

When inorganic pigments treated with the fluorine-containing silane compound of the present invention are incorporated in coating 15 compositions, the pigments are well dispersed and stable coating compositions are obtained. Inorganic pigments treated with the fluorine-containing silane compound of the present invention are superior in whiteness in the case of white pigment, tinting strength and hiding power. Treatment of inorganic pigments with the fluorine- 20 containing silane compound of this invention has been explained in the above.

Example 46

While 100 parts by weight of titanium oxide pigment was being agitated at high speed by a Henschel mixer, a solution of 0.1 part by 25 weight of



in 10 parts by weight of acetone was added to the pigment dropwise. After the addition thereof was finished, the mixture was kept at 150°C for removing the solvent. The pigment was repulverized by a fluid 30 jet mill and thus a titanium oxide pigment treated with the fluorine-containing silane compound of the present invention was obtained. This titanium oxide pigment was mixed with the materials listed below (Formula 1) and a white paint was obtained.

Formula 1

<u>Ingredient</u>	<u>parts by weight</u>
Treated titanium oxide pigment	30
"Lumiflon LF-200C" (a fluorine resin solution supplied by Asahi Glass Co., solid content 60%)	142.9
Xylene	35.7
Methylisobutylketone	107.1
Isocyanate (hardener)	13.3

10 This coating composition was applied on hiding power testing paper to a thickness of 0.00254cm (10mil). The thus coated paper was used as a test specimen and the L, a, b values of the white part thereof were measured. The whiteness was calculated as $100 - \sqrt{(100-L)^2 + a^2 + b^2}$. Then gloss at 60° of the white part was measured by a gloss meter, and the hiding ratio ((reflectivity of black part)/(reflectivity of white part)) was determined by a reflectometer. Further, a black paint of the same formula as above in which 1.5 parts by weight of carbon black was used instead of 30 parts by weight of titanium white was prepared. Thirty (30) parts by weight of the black paint was mixed with 100 parts by weight of the above described white paint and the tinting strength of the white paint was checked. The results are shown in Table 20.

Comparative Example 35

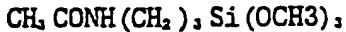
25 A white paint of Formula 1, in which untreated titanium oxide was used, was prepared and its whiteness, 60° gloss, hiding power, tinting strength were checked in the same manner as in Example 46. The results are shown in Table 20.

Example 47

30 In a solution of 10 parts by weight of $C_4F_9SO_2N(CH_3)_2CH_2CH_2Si(OCH_3)_2$, in 300 parts by weight of ethanol, 100 parts by weight of titanium oxide was dispersed in the same manner as in Example 46 and thus titanium oxide which was treated with said fluorine-containing silane compound was obtained. A white paint was prepared in accordance with the formula and procedures as described in Example 46. The same test as in Example 46 were carried out with respect to specimens coated with this white paint. The results are shown in Table 20.

Comparative Example 36

A white paint was prepared in the same manner as in Example 47 except that non-fluorine containing



5 was used as a surface treatment agent. The same test as in Example 46 were carried out with respect to specimens coated with this white paint. The results are indicated in Table 20.

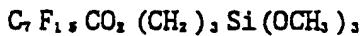
Example 48

Thirty (30) parts by weight of titanium oxide was dispersed in
10 114.2 parts by weight of toluene and 6 parts by weight of
 $\text{C}_8\text{F}_{17}\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$

was added to the dispersion and the mixture was mixed and stirred for 60min. After 171.5 parts by weight of a fluorine resin solution ("Lumiflon LF-100", a fluorine resin solution marketed by Asahi Glass Co., solid content 50%) was added and the mixture was stirred for 60min, 5.2 parts by weight of melamine was added and the mixture was stirred for 15min and thus a white paint was obtained. A test specimen was prepared by applying this paint on a polished steel sheet to the thickness of 70g/m² and baking the coated sheet at 200°C for 5min. The whiteness, 60° gloss, hiding power and tinting strength were measured. The results are shown in Table 20.

Reference Example

One hundred (100) parts by weight of calcium carbonate powder was dispersed in a solution of 5 parts by weight of



in 300 parts by weight of ethanol and the dispersion was stirred for 60min. Calcium carbonate powder treated with said fluorine-containing silane compound was obtained by filtration and drying. A white paint was prepared by mixing this calcium carbonate powder with the materials listed below (Formula 2).

Formula 2

<u>Ingredient</u>	<u>parts by weight</u>
Treated calcium carbonate powder	25
Titanium oxide	5
"Lumiflon LF-100" (a fluorine resin solution marketed by Asahi Glass Co., solid content 50%)	171.2
Toluene	114.2
Melamine (hardener)	5.2

10 This white paint was applied on the surface of hiding power test paper and the paper was baked at 130°C for 40min. Whiteness, 60° gloss, hiding power and tinting strength of this paint were measured in the same manner as in Example 46.

15

Table 20

<u>Example</u>		<u>Whiteness</u>	<u>60° gloss</u>	<u>Hiding powder</u>	<u>Tinting strength*</u>
Ex.	46	88	78	92	125
	47	87	77	91	125
20	48	88	80	-	118
	51	85	75	90	-
Comp. Ex.	35	84	74	82	100
	36	85	75	85	107
	39	84	72	85	-

25

* Numbers represent values when it is assumed that the tinting strength with respect to untreated pigment is 100.

Examples 49

30 Red iron oxide was treated with
 $C_4F_9N(CH_3)CH_2CH_2Si(OCH_3)_3$,
in the same manner as in Example 48 and mixed with the materials listed below (Formula 3) to prepare a paint.

35

Formula 3

<u>Ingredient</u>	<u>parts by weight</u>
Treated pigment	2
Carcium carbonate	10
Toluene	50
"Lumiflon LF-100" (a fluorine resin solution supplied by Asahi Glass Co., solid content 50%)	40
Isocyanate (hardener)	3.7

10 The paint was applied on a 50mmx150mm slate board to a thickness of 150g/m². The thus prepared test specimen was tested by a colorimeter to measure L, a and b values. The color difference ΔE between the case when titanium oxide was added and the case when it was not added was calculated as $\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$.

15 A paint was prepared in the same manner as above except that untreated red iron oxide was used. The color difference $\Delta E'$ was measured with respect to a specimen which was prepared in the same manner as above. The value $\Delta E/\Delta E'$ was indicated in Table 21 as an index of tinting strength of treated pigment. Generally, when this 20 value is smaller than 1 and that it is more smaller, the tinting strength is smaller. The $\Delta E/\Delta E'$ value of this pigment was 0.85 as shown in Table 21.

Example 50

25 A paint was prepared in the same manner as in Reference Example except that black iron oxide treated with 10% of $C_6F_{17}SO_2N(C_6H_5)CH_2CH_2CH_2Si(OCH_3)_3$,

was used and tested in the same manner. The $\Delta E/\Delta E'$ value was 0.95.

Comparative Example 37

30 A paint was prepared in the same manner as in Reference Example except that red iron oxide treated with 0.1% of $C_6H_5Si(OCH_3)_3$,

was used and tested in the same manner. The $\Delta E/\Delta E'$ value was 0.98.

Comparative Example 38

35 A paint was prepared in the same manner as in Reference Example except that black iron oxide treated with 10% of $CH_2CONH(CH_3)_2Si(OCH_3)_3$,

was used and tested in the same manner. The $\Delta E/\Delta E'$ value was 0.95.

The results of Example 49 through Comparative Example 38 are summarized in Table 21.

Table 21

Ex.	Pigment	F-containing silane	Amount	$\Delta E/\Delta E'$
49	Red iron oxide	$C_6F_{11}SO_2N(CH_3)(CH_2)Si(OCH_3)_3$	0.1	0.85
50	Black iron oxide	$C_6F_{11}SO_2N(C_6H_5)(CH_2)Si(OCH_3)_3$	10.0	0.75
10 Comp. Ex.				
37	Red iron oxide	$C_6H_5Si(OCH_3)_3$	0.1	0.95
38	Black iron oxide	$CH_3CONH(CH_2)Si(OCH_3)_3$	10.0	0.95

Example 51

15 A super-fine silica powder ("Aerosil #200" marketed by Nippon Aerosil Kabushiki Kaisha), which is a paint additive having thickening effect, was treated with 3.0% by weight of the fluorine-containing silane compound used in Example 47, that is,
 $C_6F_{11}SO_2N(CH_3)CH_2CH_2CH_2Si(OCH_3)_3$,
20 and a paint was prepared using the materials listed below (Formula 4).

Formula 4

Ingredient	parts by weight
Treated super fine silica powder	2
titanium oxide pigment	10
"Lumiflon LF-300" (a low viscosity fluorine resin solution marketed by Asahi Glass Co.)	30
Toluene	60
Isocyanate (hardener)	2.8

With respect to this paint, the same test as employed in Example 46 was carried out. The results are indicated in Table 20.

Comparative Example 39

35 A paint was prepared in the same manner as in Example 51 except that untreated super-fine silica powder was used and the paint was tested in the same manner. The paint of Example 51 was superior to that of this comparative example by 2.3% in whiteness, by 3.6% in 60°

gloss and by 8.4% in hiding power.

These paints were centrifuged and allowed to stand for checking the settling property. The paint prepared using the super-fine silica powder treated with the fluorine-containing silane compound did not settle when it was centrifuged at 1000rpm for 30min. The paints prepared using the untreated super-fine silica powder was settled under the same condition. It was proved that the super-fine silica powder treated with the fluorine-containing silane compound of the present invention was superior in thickening property to that prepared with the untreated super-fine silica powder.

The fluorine-containing silane compounds of the present invention improve water- and oil-repellency, staining resistance, resistance to organic solvents of wax when they are added thereto. For this purpose, the compounds are added to wax in an amount of 0.1 to 20% by weight of wax, preferably 1 to 5% by weight. Usually the compounds are admixed with wax in the form of a melt. However, it can be admixed with wax in the form of a solution in a suitable solvent.

Example 52

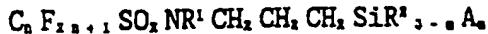
3.5g of
 $\text{C}_8\text{F}_{17}\text{SO}_3\text{N}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$,
 was admixed with melt of 100g of a commercially available wax ("Hoechst Wax S" marketed by Nippon Hoechst Kabushiki Kaisha) and the mixture was applied on the surface of a 5mm thick slide glass. The contact angles for water and liquid paraffin were measured. They were respectively 123° and 82°. Those of the neat wax were 91° and 28° respectively.

Comparative Example 40

The procedures of Example 52 were repeated with respect to a commercially available fluorine containing surfactant ("EFTOP-201" marketed by New Akita Chemical Co.) instead of said fluorine containing silane compound and the contact angles of the thus modified wax were 101° for water and 45° for liquid paraffin.

What we claim is:

1. An N-alkyl-N-[3-(substituted-silyl)propyl]-perfluoroalkyl-sulfonamide represented by the formula



5 wherein R¹ is an alkyl group having 1-5 carbon atoms, R² is an alkyl group having 1-5 carbon atoms, A is a group selected from chlorine, bromine and an alkoxy group having 1-5 carbon atoms, n is an integer of 4-12 and m is an integer of 1-3.

10 2. The compound recited in Claim 1, wherein A is methoxy, ethoxy or chlorine.

3. The compound recited in Claim 1, wherein n is an integer of 6-10.

4. The compound recited in Claim 3, wherein n is 8.

5. The compound recited in Claim 1, wherein R¹ is propyl.

6. The compound recited in Claim 1, wherein R² is methyl or ethyl.

15 7. The compound recited in Claim 1, wherein m is 3.

8. The compound recited in Claim 1, which is N-n-propyl-N-[3-(trichlorosilyl)propyl]-perfluorooctylsulfonamide.

9. The compound recited in Claim 1, which is N-n-propyl-N-[3-(trimethoxysilyl)propyl]-perfluorooctylsulfonamide.

20 10. A process for preparing N-alkyl-N-[3-(substituted-silyl)-propyl]-perfluoroalkylsulfonamide represented by the formula



wherein R¹ is an alkyl group having 1-5 carbon atoms, R² is an alkyl group having 1-5 carbon atoms, A is a group selected from chlorine, bromine and an alkoxy group having 1-5 carbon atoms, n is an integer of 4-12 and m is an integer of 1-3, comprising reacting a compound represented by the formula



wherein R¹ and n are as defined above, with a compound represented by the formula



wherein R², A and m are as defined above, in the presence of an addition catalyst.

35 11. The process recited in Claim 10, wherein the addition catalyst is a compound selected from chloroplatinic acid, azo- bis-isobutyronitrile, benzoyl peroxide, an octacarbonyl complex of cobalt, platinum or rhodium.

12. The process recited in Claim 10, wherein, when A is chlorine or

bromine, the addition product is further reacted with an alcohol having 1-5 carbon atoms.

13. The process recited in Claim 12, wherein the reaction of the addition product and the alcohol is conducted by blowing dry air into the reaction mixture.

14. The process recited in Claim 12, wherein the reaction of the addition product and the alcohol is conducted under a reduced pressure.

15. The process recited in Claim 10, wherein, when A is chlorine or bromine, the addition product is further reacted with an alkoxide of an alcohol having 1-5 carbon atoms.

16. The process recited in Claim 10, wherein, when A is chlorine or bromine, the addition product is further reacted with orthoformic acid ester of an alcohol having 1-5 carbon atoms.

17. A process for preparing N-alkyl-N-[3-(substituted-silyl)-propyl]-perfluoroalkylsulfonamide represented by the formula



wherein R¹ is an alkyl group having 1-5 carbon atoms, R² is an alkyl group having 1-5 carbon atoms, A is an alkoxy group having 1-5 carbon atoms, n is an integer of 4-12 and m is an integer of 1-3, comprising reacting a compound represented by the formula



wherein Y is fluorine, chlorine or bromine, with a compound represented by the formula



wherein R¹, R², m and A are as defined above.

18. The process as recited in Claim 17, wherein the reaction is conducted in the presence of an organic base.

19. The process recited in Claim 17, wherein pyridine or triethylamine is used as an organic amine.

20. The process recited in Claim 17, wherein the compound of formula (IV) is used in an amount of more than 1 mole equivalent to the amount of the compound of formula (V).

21. The process recited in Claim 17, wherein the compound of formula (IV) is used in an amount of 1.05 to 1.2 mole equivalent to the amount of the compound of formula (V).

22. A water- and oil-repellent for inorganic materials comprising a compound recited in any of Claims 1-9.

23. A fluorine resin composition containing inorganic filler treated with 0.1-10% by weight of a compound recited in any of Claims 1-9.

24. An inorganic powder or fiber ~~to~~ the surface of which, 0.1-20% by weight of a compound recited in any of Claims 1-9.

5 25. A metallic material the surface of which is treated with a compound recited in any of Claims 1-9.

26. A paper material the surface of which is treated with a compound recited in any of Claims 1-9.

10 27. A glass material the surface of which is treated with a compound recited in any of Claims 1-9.

28. An inorganic construction material which is treated with a compound recited in any of Claims 1-9.

29. A coating composition which contains pigment treated with 0.1-20% by weight of a compound recited in Claims 1-9.

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